

Lattice analogy of area-difference elasticity model for lipid-detergent bilayer vesiculation

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The vesiculation process was examined in the lipid-detergent solution (dimyristoyl-sn-glycero-phosphatidylcholine/octaethyleneglycol n-dodecyl ether/water), using small-angle neutron scattering experiments [1]. When observing vesiculation proceeds from rod-like micelles to unilamellar vesicles, the transformation is induced by jump-like temperature increase and a monotonic increase in detergent concentration. Our numerical estimations of the vesicle shape parameters (the elasticity coefficients and its fraction on a macroscopic scale) are based upon the area-difference elasticity model [2, 3]. Thus, we composed the numerical Monte Carlo method, which connects the macroscopic and microscopic scales by the concept of self-avoiding random surfaces.

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INTRODUCTION

We study the lyotropic processes, which are widely distributed in biological systems and define the self-organization phenomena. In lyotropic liquid crystals, the numerous examples (or even, in its clear majority), when topological genus of mesophase surfaces was changed at the phase transitions, are known.

As Kiselev observed in small-angle neutron scattering investigations [1], self-assembled vesiculation occurs between rod-like micelles and unilamellar vesicles with closed surfaces. Self-assembled vesiculation is induced by temperature jump of $100 \text{ K} \cdot \text{min}^{-1}$ from room temperature and increases as function of detergent concentration. The typical bilayer-vesicle shape dimyristoyl-sn-glycero-phosphatidylcholine/water (*DMPC/H₂O*) was observed experimentally in [4]. The different types of mesomorphism are distinguished by the nonionic surfactant influence in dimyristoyl-sn-glycero-phosphatidylcholine/octaethylene-glycol n-dodecyl ether/water (*DMPC/C₁₂E₈/H₂O*) and the drastic temperature jump.

In principle, certain closed stationary shapes (pears, prolates, oblates, stomatocytes and nonaxisymmetric shapes with the symmetry D_{2h}) are possible [2]. Theoretical models, which combine phenomenological and microcanonical methods were developed to interpret the spontaneous vesiculation phenomena in mesomorphism. Based on Helfrich theory, a spontaneous curvature c_0 (shape independent c_0 with discontinuous budding transition) model and area difference model (shape independent ΔA with continuous one). The area-difference elasticity (ADE) model [3] describes the energy as a sum of two terms: one depends on curvature at any point on the surface, and second depends on curvature-induced area difference between the inner and outer monolayers. In the bilayer-couple model by Svetina et al. [5], the bilayer structure is modelled by representing its two monolayers

as closed neutral surfaces with a constant separation distance. The elastic energy is composed of the local and nonlocal bending energies of the membrane.

MODEL OF SHAPE TRANSFORMATIONS

At a spasmodic rise in temperature, a rod-like micelle becomes unstable and transforms into a bilayer, which then collapses into a hollow sphere. Disintegration of the rod-like micelles and the bilayer were not experimentally observed [1], presumably, due to a fast jump. All of these phenomena look like a first order phase transitions, and there are situation when the symmetries of both phases are not in some ratio.

The typical budding process has been phenomenologically described [6] and the shape equation for the axisymmetric equilibrium shape was obtained from some general variational ansatz. In a pure *DMPC* solution, generative only the lamellar phase, it is found the lateral compression modulus and bilayer bending rigidity. However, at addition of nonionic surfactant $C_{12}E_8$, it becomes difficult to analytically predict the same parameters of the new mesomorphic series. Using the ADE model [5, 7] it is possible to determine the minimum energy shape of the vesicle as a function of the reduced volume $\nu = \frac{V}{V_0}$, where V is the enclosed volume and V_0 is the initial volume. The reduced volume ν is concerned with the measured hydrodynamical radius of a vesicle by certain relations [7]. To define the vesicle structure parameters, methods that combine the Helfrich spontaneous curvature theory [3, 7] and the bilayer coupling model were developed.

In terms of a microscopic canonical ensemble and lattice Ising-like models, the main mesophases structure parameters may be connected by a spontaneous curvature, which is constructed on dual lattices [8] by self-avoiding random surfaces. One would think so, that in frame of any spin variables, the mixture content is disregarding.

LATTICE MONTE CARLO METHOD

As noted by Caselle [8], a gas of self-avoiding random surfaces (SARS) with unconstrained topology and is weighted by the usual area term $e^{-\beta A}$, where A is a surface area and $\beta = 1/k_B T$ (k_B is the Boltzmann constant, T is the absolute temperature), belongs to the same class of the Ising model. As other kinds of coupling are introduced, it is possible to generate these surfaces on the body centered cubic (*bcc*) lattice and the dual lattice, like the extrinsic curvature. The reduced Hamiltonian of the Ising model has the form

$$-\beta H = \frac{\beta_h}{2} \sum_{\langle ij \rangle} \sigma_{ij} + \frac{\beta_s}{2} \sum_{\langle kl \rangle} \sigma_{kl} + \frac{\beta_t}{8} \sum_v \sigma_v \quad (1)$$

with the partition function $Z(\beta_s, \beta_h, \beta_t) = \sum_{\sigma=\pm 1} e^{-\beta H}$, where $\beta_s, \beta_h, \beta_t$ are the coefficients of couplings, $\langle ij \rangle$ and $\langle\langle kl \rangle\rangle$, $(ijkl)$ are three kinds of coupling, and $\sigma_i = -1, 0, 1$ are the spin components, which correspond to the different types of mixture molecules (lipid, surfactant and water respectively), $\sigma_v = \sigma_i \sigma_j \sigma_k \sigma_l$. The coupling coefficients are normalized by action A in terms of the Riemannian curvature R [8], which is in accordance to the Gauss-Bonnet theorem $\int d^2 \xi \sqrt{g} R = \sum_v R_v = \chi(S)$. R_i is the curvature components for four site spin configurations on the *bcc* lattice. The concentration term β_t in this model is in respect to by the chemical potential μ [9]. This treatment allow the numerical estimations to be conducted with the lattice Monte Carlo technique for the free energy and structural characteristics of the vesicular phases.

According to these calculations, all of transitions with qualitative surface changing genus, at β_t range between 0.4 and 0.8, may correspond to the appropriate transitions, found in [8] (Fig. 1.). The structure parameter of a vesicle shown at Fig. 2.

The shape function $r(\theta, \varphi)$ corresponds to the surface radius R_s for the other follows numerical simulations. This model conveniently calculates the including volume and other main structure parameters to plot the phase diagrams of lyotropic mixtures.

SUMMARY

The ADE model satisfactorily describes the vesicle phase transformations, where the non-homogeneous local properties can be expressed by the elasticity modulus and its fraction in a macroscopic scale. However, the presented model is well suited for studying numerous biophysical phenomena and complements the existing conceptions. In addition to phenomenological ADE calculations, the lattice treatment of the lyotropic phase behavior of the aggregates is essential for directly controlling the concentration, which is a determinative param-

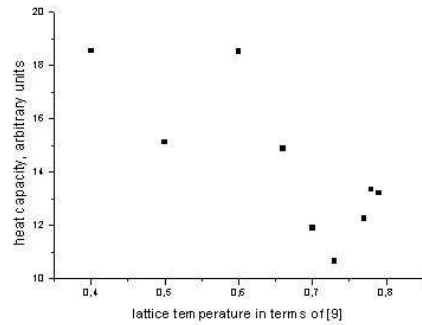


FIG. 1: The heat capacity dependence of temperature parameter β for binary mixture with nonionic surfactant, Monte Carlo error is 10^{-4}

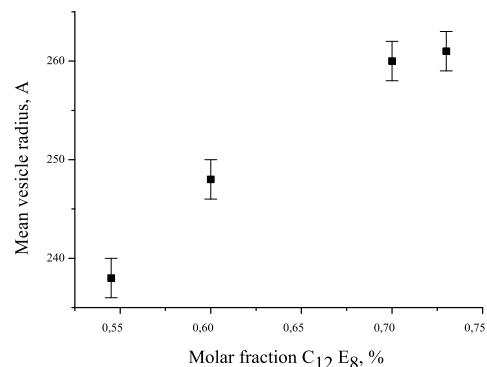


FIG. 2: Monte Carlo simulations for vesicle structural parameter (mean curvature $R(\text{\AA})$) evolution at 303 K

eter in the lyomesomorphic transformations. Computer cluster simulation analysis is useful to investigate the local curvature properties of different aggregates, including vesicles.

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